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REDOX EQUILIBRIUM OF IRON IN SILICATE GLASSES

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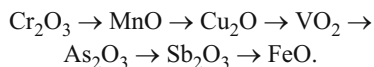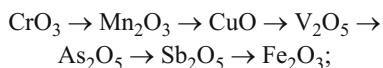
The effect of some additives on the equilibrium of valence forms of iron is investigated. It is demonstrated that tin and carbon more significantly than fluorine reduce iron. The redox potential of the glass matrix affects the equilibrium between difference valence forms of iron much less than additives correcting spectral characteristics of glass.

Glass can be clear or tinted, depending on its purpose and application area. Signaling used by railroad, automobile, or air transport is impossible without color filters with strictly specified color characteristics. About 100 varieties of tinted glass find applications in the production of precise instruments.

Coloring is imparted by *d*-elements which can exist each in several valence-coordination states and, depending on this particular state, selectively absorb light radiation in a strictly fixed spectral range. The ratio between different valence-coordination forms depends on numerous factors: glass composition, its thermal history, type of initial material, presence of extraneous inclusions, etc. [1].

When two variable-valence elements are present together, they mutually influence each other according to the following redox series [2]:

$$CrO_3 \rightarrow Mn_2O_3 \rightarrow CuO \rightarrow V_2O_5 \rightarrow$$
$$As_2O_5 \rightarrow Sb_2O_5 \rightarrow Fe_2O_3;$$

$$Cr_2O_3 \rightarrow MnO \rightarrow Cu_2O \rightarrow VO_2 \rightarrow$$
$$As_2O_3 \rightarrow Sb_2O_3 \rightarrow FeO.$$

Each higher-valence oxide in the upper series by losing part of oxygen can oxidize any oxide to the right in the lower-valence second series.

Iron is used to impart heat-shielding properties and obtain color filters selectively absorbing IR radiation or suppressing the violet part of the spectrum. This element is present in glass in two valence states: Fe(II) with an absorption band around 1000 – 1100 nm and Fe(III) with a maximum in the short-wave range near 380 – 400 nm. To obtain required spectral characteristics, it is necessary to strictly maintain the Fe(II) : Fe(III) ratio.

The purpose of the present study is to investigate the equilibrium of iron in silicate glasses.

The concentrations of bivalent and trivalent iron in tinted optical glasses were calculated based on the Russian glass catalog [3]. In these calculations the authors were guided by the spectrophotometric method for identifying colorant ions in glasses developed at the S. I. Vavilov State Optical Institute (OST 3-4728–79). The development and implementation of this method was carried out under the direction of L. I. Demkina. The method is based on the Buger – Lambert – Baire law stating that when several colorants are simultaneously present in a particular glass, the absorption coefficient a_λ of this glass for any wavelength λ is equal to the sum of the products of the specific absorption coefficient of the individual ion χ_λ by it weight content w_i in the glass:

$$a_\lambda = \sum \chi_{\lambda i}\, w_i .$$

At the same time

$$a_\lambda = \mu_\lambda - r_\lambda ,$$

where μ_λ and r_λ are the attenuation and scattering coefficients, respectively, of the glass at the wavelength λ.

Table 1 correlates the results of calculating the content of Fe(II) and Fe(III) with the total content of iron in glasses determined by synthesis. It can be seen that calculated data differ from experimental ones by 3 – 6%, consequently, the results can be regarded as reliable.

The following reaction can take place between iron and the reducing additives present in the glass melt [2]:

$$Fe_2O_3 + C(Sn) \rightleftarrows FeO + CO_2\,(SnO_2\,).$$
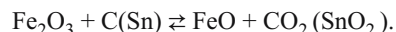
As a consequence, the equilibrium Fe(II) $\rightleftarrows$ Fe(III) changes and the spectral curve of glass related to this equilibrium changes as well.

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TABLE 1

Glass	Weight content of iron in glass, %				Calculation error $\dfrac{w_{Fe\,(tot)}}{\sum \left(w_{Fe(II)} + w_{Fe(III)} \right)} \times 100\%$
	by synthesis (total)	estimated			
		$w_{Fe(III)}$	$w_{Fe(II)}$	$\Sigma\,(w_{Fe(II)} + w_{Fe(III)})$	
SZS-5	0.707	0.704	0.577	0.731	3.4
SZS-15	0.185	0.004	0.186	0.190	2.7
NS-14	1.645	1.200	0.358	1.558	5.3

TABLE 2

Glass	$\bar{a}_\lambda$, cm^{-1}, for wavelength, nm		$d_{Fe(i)} = \dfrac{w_{Fe(i)}}{w_{Fe(II)} + w_{Fe(III)}} \times 100\%$		$w_{red} = \dfrac{w_C + w_{Sn}}{w_{Fe(tot)}}$	ROPM
	400	1000	Fe(II)	Fe(III)		
SZS-5	0.707	10.46	79	21	1.410	3.291
SZS-15	0.486	13.51	98	2	3.790	2.292
SZS-16	0.869	7.83	66	34	0.635	1.131
NS-13	4.571	2.40	18	82	0.043	0.869
NS-14	1.824	4.10	23	77	0.334	0.691

Table 2 indicates some properties of iron-bearing glasses modified by tin and carbon additives.

The listed absorption coefficient $\bar{a}_\lambda$ makes it possible to eliminate the effect of iron concentration on the spectral characteristics of glass. The content of iron in the considered glasses varies from 0.185 to 3.500% and makes it possible, as a first approximation, to estimate the equilibrium Fe(II) $\rightleftarrows$ Fe(III) based on light losses at wavelengths of 380 (400) and 1000 nm that are close to the respective absorption maximums of trivalent and bivalent iron [2]. The value $\bar{a}_\lambda$ has been calculated from the expression:

$$\bar{a}_\lambda = \frac{a_\lambda}{w_{Fe(tot)}},$$

where a_λ is the glass absorption coefficient for wavelengths 380 (400) or 1000 nm, cm^{-1} and $w_{Fe(tot)}$ is the total weight content of iron in glass based on synthesis, %.

The redox potential (ROPM) reflecting the effect of the matrix composition on the redox processes in glass is calculated from the following expression [4]:

$$K_{bas} = \frac{4.6Al_2O_3 + 4.7(K_2O + Na_2O + 0.3ZnO + 0.7CaO + 0.7PbO - Al_2O_3)}{0.82SiO_2 + [B_2O_3 - (K_2O + Na_2O + 0.3ZnO + 0.7CaO + 0.7PbO - Al_2O_3)]}.$$

The share of $d_{Fe(i)}$ was determined as the quotient of the content of iron in the particular valence (II or III) form by its total content in glass. This indicator parameter makes it possible to estimate the ROPM of glass produced in particular industrial conditions and summarizes the effect of all factors: temperature, melting conditions, batch composition, glass matrix, etc. [5].

The content of reducing agents w_{red} indicated in Table 2 is the total content of carbon and tin per 1% iron. This parameter should be closely related to the Fe(II) $\rightleftarrows$ Fe(III) equilibrium.

It clearly follows from Table 2 that the specified parameters for glass NS-13 are maximal in the violet spectrum range (400 nm) and minimal in the red spectrum (1000 nm). Consequently, the content of Fe(III) ($d_{Fe(i)}$) in glass NS-13 with respect to the total iron dissolved in glass ought to be the highest and the share of Fe(II) should be the lowest. The ratio in glass SZS-15 judging from the value $\bar{a}_\lambda$ ought to be the opposite: the share of bivalent iron is maximal and the share of trivalent iron is minimal. The calculation results validate these assumption. According to ascending values of $\bar{a}_\lambda$, $d_{Fe(i)}$, ROPM, and w_{red}, glasses listed in Table 2 are ranked in the following series:

$$\bar{a}_\lambda \; (400 \text{ nm}): \quad \text{NS-13} \to \text{NS-14} \to \\ \text{SZS-16} \to \text{SZS-5} \to \text{SZS-15}; \qquad (1)$$

$$d_{Fe(III)}: \quad \text{NS-13} \to \text{NS-14} \to \\ \text{SZS-16} \to \text{SZS-5} \to \text{SZS-15}; \qquad (2)$$

$$\bar{a}_\lambda \; (1000 \text{ nm}): \quad \text{SZS-15} \to \text{SZS-5} \to \\ \text{SZS-16} \to \text{NS-14} \to \text{NS-13}; \qquad (3)$$

$$d_{Fe(II)}: \quad \text{SZS-15} \to \text{SZS-5} \to \\ \text{SZS-16} \to \text{NS-14} \to \text{NS-13}; \qquad (4)$$

$$\text{ROPM}: \quad \text{SZS-5} \to \text{SZS-15} \to \\ \text{SZS-16} \to \text{NS-13} \to \text{NS-14}; \qquad (5)$$

$$\bar{w}_{red}: \quad \text{SZS-15} \to \text{SZS-5} \to \\ \text{SZS-16} \to \text{NS-14} \to \text{NS-13}. \qquad (6)$$

Comparing series (1) and (2), (3) and (4), is a proportional dependence is obvious between the glass absorption coefficients in the red and violate spectrum ranges and the calculated shares of bivalent and trivalent iron. There is no obvious correlation between the ROPM and the Fe(II) $\rightleftarrows$ Fe(III) equilibrium: series (2), (4), and (5).

A comparison of series (4) and (6) shows that the share of bivalent iron (and the reducing potential of glass that is related to it) [5] grows symbately to the increasing relative concentration of the reducing agents in glass. Consequently, the Fe(II) $\rightleftarrows$ Fe(III) equilibrium is shifted to the left and the more so, the more reducing agents we have per 1% iron.

Table 3 gives some characteristics of iron-tinted fluorine-bearing glasses.

TABLE 3

Glass	Weight content by synthesis $Fe_{(tot)}$, %[*]	a_λ, cm^{-1}, for wavelength, nm		$\bar{a}_\lambda$, cm^{-1}, for wavelength, nm		$d_{Fe(II)}$, %[**]	ROPM of glass	$\dfrac{w_F}{w_{Fe(tot)}}$
		380	1000	380	1000			
NS-6	0.686	1.27	1.6	1.851	2.33	35	0.869	3.36
NS-7	1.155	2.20	2.4	1.905	2.08	32	0.870	1.99
NS-8	1.680	4.40	4.9	2.619	2.92	33	0.870	1.37
NS-9	2.422	8.90	6.6	3.675	2.73	26	0.870	0.95
NS-10	3.353	13.20	11.0	3.937	3.28	27	0.870	0.69
NS-11	4.445	30.00	12.9	6.749	2.90	19	0.870	0.52
NS-12	5.768	53.00	17.5	9.189	3.03	17	0.870	0.40

[*] Fluorine content in all cases was 2.3%.

[**] Calculated data.

As the value $\bar{a}_{380}$ decreases and $\bar{a}_{1000}$ increases, the considered glasses are ranked in the following series:

$$\bar{a}_{380}: \quad \text{NS-12} \to \text{NS-11} \to \text{NS-10} \to$$
$$\text{NS-9} \to \text{NS-8} \to \text{NS-7} \to \text{NS-6}; \qquad (7)$$

$$\bar{a}_{1000}: \quad \text{NS-7} \to \text{NS-6} \to \text{NS-9} \to \text{NS-11} \approx$$
$$\text{NS-8} \leftarrow \text{NS-12} \leftarrow \text{NS-10}. \qquad (8)$$

Obviously, series (7) and (8) are not totally identical. This is due to the fact that cobalt is additionally introduced in some of considered glasses in order to correct the spectral curve. It is known that iron is present in two valence states whose equilibrium depends on the glass composition, iron concentration, melting temperature, and the presence of oxidizers, reducing agents, and other variable-valence elements in the batch. Cobalt in glass keeps its constant valence equal to 2 and, depending on the glass composition, is coordinated by four or six oxygen atoms [2]. Both forms have absorption bands in the visible spectrum range and insignificant absorption in the adjacent ranges. At the same time, the practice shows that for the wavelength of 380 nm cobalt absorption is about 3 times lower than at 1000 nm. Therefore, series (7) better than series (8) reflects the Fe(II) $\rightleftarrows$ Fe(III) equilibrium.

On this basis it can be assumed that the share of trivalent iron decreases and the share of bivalent iron grows in accor-

dance with series (7). The results of computing the share of Fe(II) corroborate this assumption: the values $d_{Fe(II)}$ and $\bar{a}_{380}$ are related by a clear inverse proportion.

It follows from Table 3 that the ROPM of all glasses is equal, however, their content of Fe(II) varies from 17 to 35%. Consequently, same as in the cases of using carbon and tin additives, the ROPM has a significantly lower effect on equilibrium than fluorine, which corrects the spectral characteristics of glass. The fluorine-bearing compound Na_2SiF_6 introduced as a melting catalyst in the batch for thermally polished sheet glass increases the reducing potential of the melt and shifts the Fe(II) $\rightleftarrows$ Fe(III) equilibrium to the left [6].

In order to estimate the effect of fluorine in the considered glasses, let us compare $d_{Fe(II)}$ with the relative concentration of fluorine per 1% iron dissolved in glass $\dfrac{w_F}{w_{Fe(tot)}}$. As this parameter varies, all considered glasses are ranked in the following series (the numbers under the glass grades denote their content of lower iron):

$$\begin{array}{ccccc} \text{NS-6} \to & \text{NS-7} \to & \text{NS-8} \to & \text{NS-9} \to \\ 35 & 32 & 33 & 26 \end{array}$$
$$\begin{array}{ccc} \text{NS-10} \to & \text{NS-11} \to & \text{NS-12}. \\ 27 & 19 & 17 \end{array}$$

Obviously, the reducing potential of tinted fluorine-bearing silicate optical color filters intensifies with a growing re-

TABLE 4

Glass	Weight content, %			Relative concentration			$d_{Fe(II)}$, %
	C	Sn	F	$\dfrac{w_C + w_{Sn}}{w_{Fe(tot)}}$	$\dfrac{w_F}{w_{Fe(tot)}}$	$\dfrac{w_F + w_C + w_{Sn}}{w_{Fe(tot)}}$	
SZS-5	0.50	0.50	–	1.414	–	–	79
NS-8	–	–	2.30	–	1.369	–	33
SZS-15	0.40	0.30	–	3.784	–	–	98
NS-6	–	–	2.30	–	3.353	–	35
SZS-16	0.30	0.30	0.41	0.635	0.433	1.069	66
NS-9	–	–	2.30	–	0.950	–	26
NS-10	–	–	2.30	–	0.686	–	27
NS-13	0.15	–	2.30	0.043	0.657	0.700	18
NS-14	0.50	0.05	–	0.334	–	–	23
NS-12	–	–	2.30	–	–	0.399	17

lative concentration of fluorine; this agrees with the data in [6].

Table 4 compares some characteristics of tinted optical iron-bearing glasses that contain carbon, tin, and fluorine, which are reducing agents.

Glasses with close relative concentrations of the reducing components are arranged pairwise. Evidently, tin and carbon (in the form of coal or sugar) are stronger reducing agents than fluorides.

Thus, the ROPM of glass has a significantly lower impact on the equilibrium between the different valence forms of iron than additives correcting the spectral characteristics of glass. The more is the amount of reducing agents (carbon, tin) and fluorine per 1% iron, the more perceptible is the shift of the $Fe(II) \rightleftarrows Fe(III)$ equilibrium to the left. Tin and carbon reduce iron more intensely than fluorine does.

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